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(54) Title: HYDROFORMYLATION USING MULTIDENTATE PHOSPHITE LIGANDS

(57) Abstract: A process for hydroformylating acyclic monoethylenically unsaturated compounds to corresponding terminal aldehydes using a Group VIII transition metal and selected multidentate phosphite ligands.

TITLE

HYDROFORMYLATION USING MULTIDENTATE PHOSPHITE LIGANDS

5

FIELD OF THE INVENTION

This invention relates to a process for the preparation of linear aldehydes by hydroformylation of C₂ to C₂₀ monoethylenically unsaturated organic compounds in the presence of a Group VIII transition metal and selected multidentate phosphite ligands. The invention also relates to the selected multidentate phosphite ligands themselves, as well as hydroformylation catalysts made therefrom.

15

BACKGROUND OF THE INVENTION

Phosphorus-based ligands are ubiquitous in catalysis and are used for a number of commercially important chemical transformations. Phosphorus-based ligands commonly used in catalysis include phosphines and phosphites. These ligands include monophosphine and monophosphite ligands, which are compounds that contain a single phosphorus atom that serves as a donor to a transition metal, and bisphosphine, bisphosphite, and bis(phosphorus) ligands, which contain two phosphorus donor atoms and normally form cyclic chelate structures with transition metals.

An industrially important catalytic reaction using phosphorus-based ligands is olefin hydroformylation. Phosphite ligands are particularly good ligands for these reactions. For example, U.S. Patent 5,235,113 describes a hydroformylation process in which an organic bidentate ligand containing two phosphorus atoms linked with an organic dihydroxyl bridging group is used in a homogeneous hydroformylation catalyst system also comprising rhodium. This patent describes a process for

preparing aldehydes by hydroformylation of ethylenically unsaturated organic compounds, for example 1-octene or dimerized butadiene, using the above catalyst system. The use of phosphite ligands with rhodium has been disclosed in the hydroformylation of functionalized ethylenically unsaturated compounds. See for example Cuny et al., *J. Am. Chem. Soc.*, 1993, 115, 2066; U.S. Patents 4,769,498, 4,668,651, 4,885,401, 5,113,022, 5,059,710, 5,235,113, 5,264,616, and 4,885,401; and published international applications WO9303839, and WO9518089.

Hydroformylation processes involving organic bidentate ligands containing an aromatic dihydroxyl bridging group and terminal aryl groups bearing heteroatom substituents are described in German Patent Application DE 19717359 A1.

Hydroformylation processes involving organic bidentate ligands containing two trivalent phosphorus atoms, in which the two phosphorous atoms are linked with a 2,2'-dihydroxyl-1,1'-binaphthalene bridging group, are described in U.S. Patent 5,874,641 and the prior art referenced therein. U.S. Patent 5,874,641 describes ligands containing substituents such as esters or ketones on the 3,3'-positions of the 2,2'-dihydroxyl-1,1'-binaphthalene bridging group. Such ligands provide reasonably good selectivity in the hydroformylation of internal olefins to terminal aldehydes.

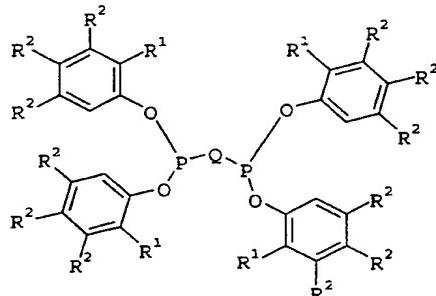
Although some of these prior art systems involve commercially viable catalysts, there remains a need for even more effective catalysts to achieve even greater commercial potential. An object of this invention is to provide such improved catalysts for hydroformylation.

SUMMARY OF THE INVENTION

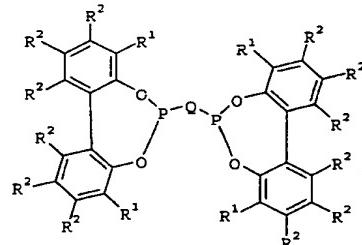
In one aspect, the present invention is a process for converting a C₂ to C₂₀ acyclic monoethylenically unsaturated compound to its corresponding terminal aldehyde, comprising reacting the compound with CO and H₂ in the presence of a Group VIII transition metal and at least one multidentate phosphite ligand of the following formulae I, II or III:

10

I

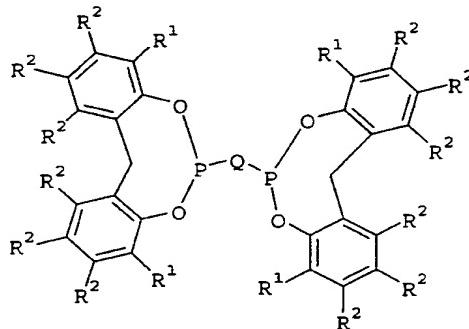


II



15

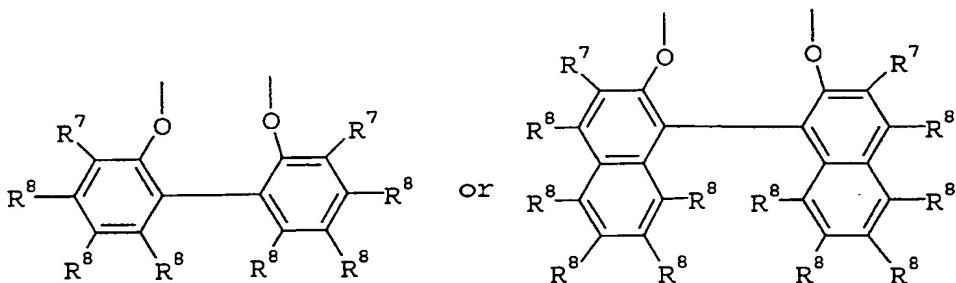
III



wherein:

- each R¹ independently is C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, F, Cl, -CO₂R⁴, -OR⁴, or -R³Z, provided that at least one R¹ is -R³Z;
- each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;
- each R³ independently is C₁ to C₁₀ alkylene;

each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;
 each Z is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)SR⁴, -SR⁴,
 5 -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶,
 -C(R⁵)=NR⁶, -C(R⁵)=N-O-R⁶, -P(O)(OR⁴)(OR⁴), -S(O)₂R⁴,
 -S(O)R⁴, -C(O)OC(O)R⁴, -NR⁴CO₂R⁴, -NR⁴C(O)NR⁵R⁶, or
 -CN;
 each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;
 10 each R⁵ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;
 each R⁶ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;
 Q is a divalent bridging group of the formula:



15 wherein:
 each R⁷ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, -CF₃, -C(R⁵)=NR⁶, -NR⁵R⁶ or -R³Z; and
 20 each R⁸ is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

The term "aryl" is meant to denote an organic radical which is derived from an aromatic hydrocarbon by removal of one atom. Suitable aryl radicals are, for example, phenyl, benzyl, naphthyl, binaphthyl, and anthracenyl.
 25 The terms "alkyl" and "alkylene" are meant to denote both straight and branched groups.

In another aspect, this invention provides for the above multidentate phosphite ligands and catalyst compositions made therefrom.

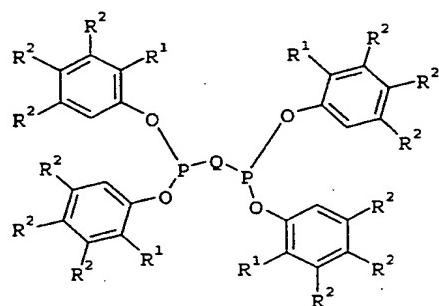
Any of the above ligands optionally may be attached 5 to a soluble or insoluble inert support. An example of an insoluble inert support is Merrifield's resin (a functionalized polystyrene resin commercially available from Aldrich Chemical Company).

10 DETAILED DESCRIPTION OF THE INVENTION

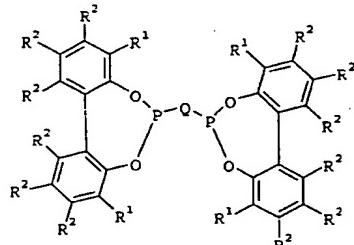
This invention provides a process for the preparation of terminal aldehydes with high catalyst performance (selectivity and/or activity). The advantages of the present process are particularly pronounced when the 15 reactant is an internally monoethylenically unsaturated compound. Preparing terminal aldehydes starting from internally monoethylenically unsaturated compounds using previously known hydroformylation processes generally results in moderate selectivity to terminal aldehydes, 20 some hydrogenation of the double bond and/or lower catalytic activity. An additional advantage of the process according to the present invention is that the linearity [terminal aldehydes/(terminal + branched 25 aldehydes)] is high, facilitating the isolation of the desired terminal aldehyde from a mixture of terminal and branched aldehydes.

The catalyst compositions useful in the processes of the invention comprise selected multidentate phosphite ligands and a Group VIII transition metal, which is 30 provided in the form of a chemical compound.

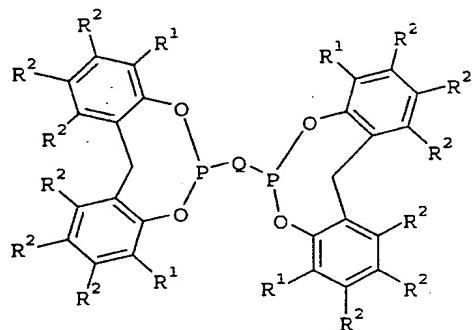
The multidentate phosphite ligand is of the formulae I, II or III:



I



II



5

III

wherein:

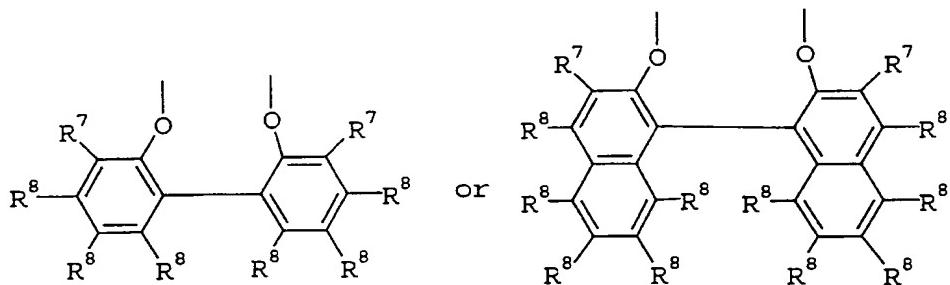
- each R¹ independently is C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, F, Cl, -CO₂R⁴, -OR⁴, or -R³Z, provided that at least one R¹ is -R³Z;
- each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;
- each R³ independently is C₁ to C₁₀ alkylene;
- each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;
- each Z is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)SR⁴, -SR⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, -C(R⁵)=NR⁶, -C(R⁵)=N-O-R⁶, -P(O)(OR⁴)(OR⁴), -S(O)₂R⁴, -S(O)R⁴, -C(O)OC(O)R⁴, -NR⁴CO₂R⁴, -NR⁴C(O)NR⁵R⁶, or -CN;

each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;

each R⁵ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;

5 each R⁶ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;

Q is a divalent bridging group of the formula:



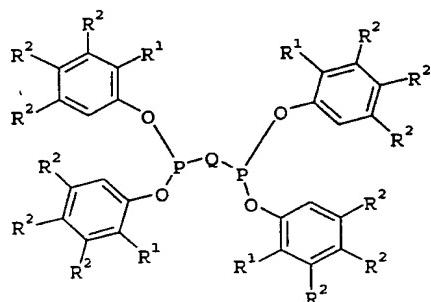
wherein:

10 each R⁷ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, -CF₃, -C(R⁵)=NR⁶, -NR⁵R⁶ or -R³Z; and

each R⁸ is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

15 Preferred multidentate phosphite ligands are of the following formula I:

I



wherein:

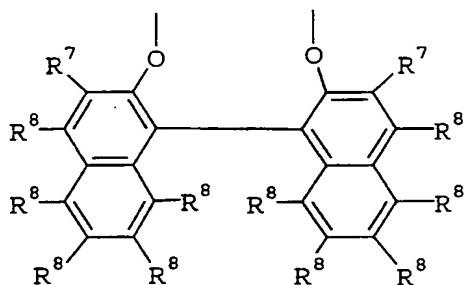
each R¹ independently is -R³Z;

each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;

5 each R³ independently is C₁ to C₄ alkylene;

each Z independently is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, or -C(R⁵)=NR⁶;

10 Q is a divalent bridging group of the formula:



wherein:

each R⁷ independently is -CO₂R⁴, -C(O)R⁴,

-C(R⁵)=N-O-R⁶, -CHO, -CN, or -C(R⁵)=N(R⁶); and

15 each R⁸ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

The multidentate phosphite ligands of the present invention can be prepared by using a process in which a phosphorochloridite is reacted with a divalent bridging group. The phosphorochloridite can be prepared by treating at a temperature between about -40°C and 10°C one molar equivalent of PCl₃ with about two molar equivalents of substituted phenol in the absence of an organic base. The resulting solution is then treated with at least two equivalents of an organic base to produce a phosphorochloridite. When the substituted phenols are replaced with substituted biphenol or substituted alkylidenebisphenol, the phosphorochloridite is similarly prepared from initially mixing one molar equivalent of PCl₃ with about one molar equivalent of substituted

biphenol or substituted alkylidenebisphenol between about -40°C and 10°C in the absence of an organic base. The resulting solution is then treated with at least two equivalents of an organic base to produce a

5 phosphorochloridite.

When preparing the phosphorochloridite in the above manner, it is important to maintain temperature in the -40°C and 10°C range during the base addition. The addition of base results in the formation of an insoluble salt

10 formed by neutralizing HCl, and the reaction mixture can become a thick slurry. Such a slurry can create problems in achieving good mixing of base which is important in avoiding temperature gradients in the reaction mixture which can decrease yield of the desired product. It is

15 important, therefore, that the reaction be conducted with vigorous stirring or other agitation to allow effective removal of heat from the reaction mixture. Cooling to the required temperature range can be accomplished by well-known techniques in the art.

20 At a temperature range between -40°C and 70°C, the phosphorochloridite is reacted with about a half molar equivalent of the divalent bridging group. If less than three equivalents of the organic base were utilized in preparing the phosphorochloridite, additional organic

25 base is added to bring the total equivalents of organic base utilized in the process to at least three.

The base used in preparing the multidentate phosphite ligands should be anhydrous and soluble in the reaction medium. Suitable bases are organic amines. Especially

30 preferred are trialkylamines. The most preferred bases are selected from the group consisting of tributylamine, benzyldimethylamine, triethylamine, and diisopropylmethylamine.

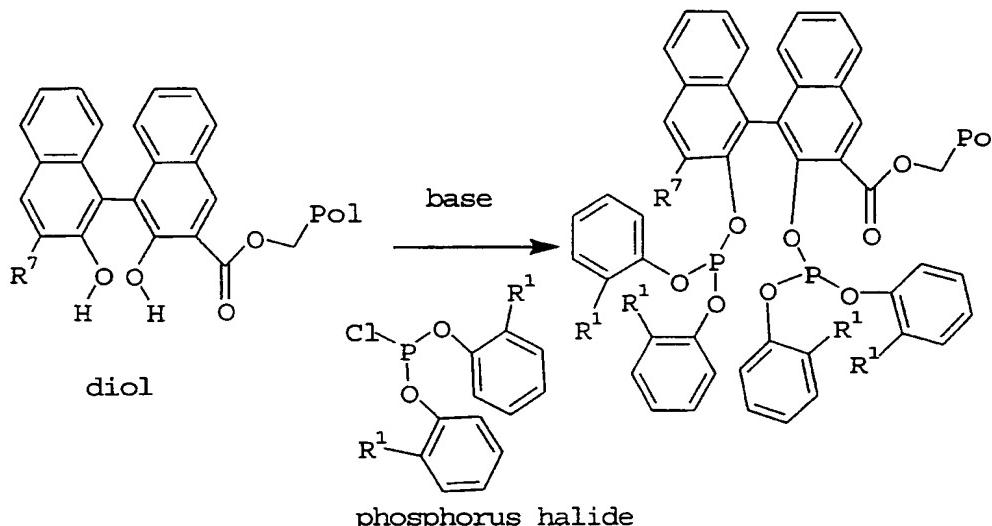
35 The phosphorochloridites can be prepared by a variety of other methods known in the art. One method involves treating phenols with PCl₃, such as described in, *Polymer 1992, 33, 161; Inorganic Syntheses, 1966, 8, 68; U.S.*

Patent No. 5,210,260; and Z. Anorg. Allg. Chem., 1986, 535, 221.

When the phosphorochloridite cannot be prepared in good yield from PCl_3 , the preferred method involves the treatment of N,N-dialkyl diarylphosphoramidite derivatives with HCl. The N,N-dialkyl diarylphosphoramidite is of the form $(\text{R}^9)_2\text{NP}(\text{aryloxy})_2$, where R^9 is a C_1 to C_4 alkyl group, and can be obtained by reacting phenol or substituted phenol with $(\text{R}^9)_2\text{NPCl}_2$ by methods known in the art, such as described in WO9622968, U.S. Patent 5,710,306, and U.S. Patent 5,821,378. The N,N-dialkyl diarylphosphoramidites may be prepared, for example, as described in Tet. Lett., 1993, 34, 6451; Synthesis, 1988, 2, 142-144, and Aust. J. Chem., 1991, 44, 233.

The multidentate phosphite ligand does not have to be pure to be used in the process of the present invention; it can contain some monodentate phosphites as impurities.

Multidentate phosphite ligands may be supported on soluble or insoluble inert supports. Polymer-supported multidentate phosphorus ligands may be prepared by a variety of methods known in the art. See WO9303839, U.S. Patents 4,769,498 and 4,668,651, and WO9906146. In general, the preparation involves the reaction of a phosphorus halide, typically but not limited to, chloride, with a diol to form P-O bonds. A representative example is shown below.



"Pol" denotes the soluble or insoluble inert support.

R¹ and R⁷ are as defined above.

A specific example of an insoluble inert support is
 5 Merrifield's resin (a functionalized polystyrene resin available from Aldrich Chemical Company). The above diol may be prepared by first partial esterification of 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylic acid with Merrifield's resin, followed by esterification of the
 10 resulting ester/acid diol intermediate. The esterification conditions are well known to those skilled in the art of organic synthesis.

The invention also provides for certain multidentate phosphite ligands and catalyst compositions made therefrom. In particular, these include the ligands of Formula I, II or III and the combination of a ligand of Formula I, II or III with a Group VIII transition metal compound. Preferred Group VIII transition metals are rhodium, cobalt, iridium, palladium and platinum, the
 15 most preferred being rhodium. The Group VIII metal is provided in the form of a compound, such as a hydride, halide, organic acid salt, ketonate, inorganic acid salt, oxide, carbonyl compound or amine compound. Preferred Group VIII metal compounds are Ir₄(CO)₁₂, IrSO₄, RhCl₃,

Rh(NO₃)₃, Rh(OAc)₃, Rh₂O₃, Rh(acac)(CO)₂, [Rh(OAc)(COD)]₂, Rh₄(CO)₁₂, Rh₆(CO)₁₆, RhH(CO)(Ph₃P)₃, [Rh(OAc)(CO)₂]₂, and [RhCl(COD)]₂ (wherein "acac" is an acetylacetone group; "OAc" is an acetyl group; "COD" is 1,5-cyclooctadiene; and "Ph" is a phenyl group). However, it should be noted that the Group VIII metal compounds are not necessarily limited to the above listed compounds. The rhodium compounds, suitable for hydroformylation, can be prepared or generated according to techniques well known in the art, as described, for example, in WO 95 30680, U.S. Patent 3,907,847, and J. Amer. Chem. Soc., 115, 2066, 1993. Rhodium compounds that contain ligands which can be displaced by the present multidentate phosphite ligands are a preferred source of rhodium. Examples of such preferred rhodium compounds are Rh(CO)₂ (acac), Rh(CO)₂(C₄H₉COCHCO-t-C₄H₉), Rh₂O₃, Rh₄(CO)₁₂, Rh₆(CO)₁₆, Rh(O₂CCH₃)₂, and Rh(2-ethylhexanoate).

The reactant of the present process is a monoethylenically unsaturated organic compound having at least one ~~☒~~ C=C~~☒~~ bond in the molecule and preferably 2 to 20 carbon atoms. Examples of suitable ethylenically unsaturated organic compounds are linear terminal olefinic hydrocarbons, for example, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene and 1-dodecene; branched terminal olefinic hydrocarbons, for example, isobutene and 2-methyl-1-butene; linear internal olefinic hydrocarbons, for example, cis- and trans-2-butene, cis- and trans-2-hexene, cis- and trans-2-octene, cis- and trans-3-octene; branched internal olefinic hydrocarbons, for example, 2,3-dimethyl-2-butene, 2-methyl-2-butene and 2-methyl-2-pentene; terminal olefinic hydrocarbons; internal olefinic hydrocarbon mixtures; for example, octenes, prepared by dimerization of butenes.

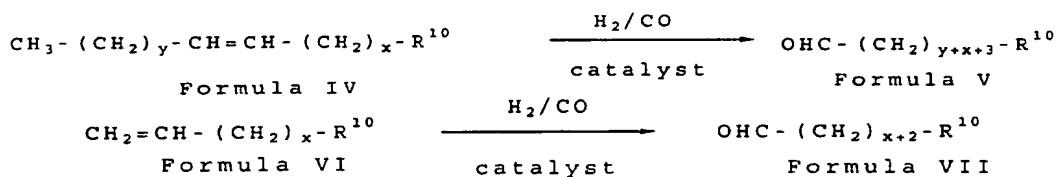
Examples of suitable olefinic compounds include those substituted with an unsaturated hydrocarbon group,

including olefinic compounds containing an aromatic substituent such as styrene, alpha-methylstyrene and allylbenzene.

The ethylenically unsaturated organic compound can be substituted with one or more functional groups containing a heteroatom, such as oxygen, sulfur, nitrogen or phosphorus. Examples of these heteroatom-substituted ethylenically unsaturated organic compounds include vinyl methyl ether, methyl oleate, oleyl alcohol, 3-pentenenitrile, 4-pentenenitrile, 3-pentenoic acid, 4-pentenoic acid, methyl 3-pentenoate, 3-pentenal, allyl alcohol, 7-octen-1-al, acrylonitrile, acrylic acid esters, methyl acrylate, methacrylic acid esters, methyl methacrylate, and acrolein.

The invention is especially directed to hydroformylation processes in which a linear aldehyde compound is prepared starting from internal monoethylenically unsaturated organic compounds with 2 to 20 carbon atoms.

Preferred monoethylenically unsaturated compounds that are useful in the process of this invention are shown in Formulas IV and VI, and the corresponding terminal aldehyde compounds produced are illustrated by Formulas V and VII, respectively.



wherein

R¹⁰ is H, -CN, -CO₂R⁵, -C(O)NR⁵R⁶, -CHO, -OR⁴, or OH;

y is an integer from 0 to 12;

x is an integer from 0 to 12;

5 R⁴, R⁵ and R⁶ are as defined above.

Particularly preferred internal monoethylenically unsaturated organic compounds are 3-pentenenitrile, 3-pentenoic acid, and alkyl 3-pentenoate, such as methyl 3-pentenoate. The linear aldehyde compound prepared by 10 the present process starting with one of these compounds can be used advantageously in the preparation of ε-caprolactam, hexamethylenediamine, 6-aminocaproic acid, 6-aminocapronitrile or adipic acid, which are precursors for Nylon-6 and/or Nylon-6,6.

15 The 3-pentenenitrile may be present in mixtures containing 4-pentenenitrile. Similarly, when alkyl 3-pentenoate or 3-pentenoic acid is the reactant used in the present process, mixtures containing alkyl 4-pentenoate or 4-pentenoic acid, respectively, may be 20 present. Because the 4-isomers of these compounds react in a similar fashion as their corresponding 3-isomers to the desired linear aldehyde, a mixture of isomers can be used directly in the present process. Hydroformylation of these 3- and 4-isomer can be carried 25 out in the presence of 2-isomers. Impurities can be present as long as they do not interfere with the reaction.

The hydroformylation process according to the invention can be performed as described below.

30 The reaction conditions of the hydroformylation process are, in general, the same as those used in a conventional process, described for example in U.S. Patent 4,769,498, and will be dependent on the particular starting monoethylenically unsaturated organic compound. 35 For example, the temperature can be from ambient temperature to 200°C, preferably from about 50 to 150°C, and more preferably from 85° to 110°C. The pressure may

vary from normal pressure to 5 MPa, preferably from 0.1 to 2 MPa. The pressure is, as a rule, equal to the combined hydrogen and carbon monoxide partial pressures.

However, extra inert gases may also be present; the

5 pressure may vary from normal pressure to 15 MPa when inert gases are present. The molar ratio of hydrogen to carbon monoxide is generally between 10:1 and 1:10, and preferably between 6:1 and 1:2.

10 The amount of transition metal compound is selected so that favorable results can be obtained with respect to catalyst activity and process economy. In general, the concentration of transition metal in the reaction medium is between 10 and 10,000 ppm and more preferably between 50 and 1000 ppm, calculated as free metal.

15 The molar ratio of phosphorus ligand to transition metal is selected so that favorable results can be obtained with respect to catalyst activity and desired aldehyde selectivity. This ratio generally is from about 0.5 to 100 and preferably from 1 to 20 (moles phosphorus per mole metal).

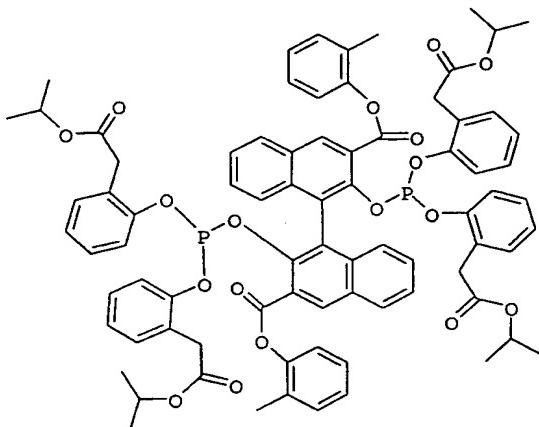
20 The solvent may be the mixture of reactants of the hydroformylation reaction itself, such as the starting unsaturated compound, the aldehyde product and/or by-products. Other suitable solvents include saturated hydrocarbons (for example, kerosene, mineral oil, or cyclohexane), ethers (for example, diphenyl ether or tetrahydrofuran), ketones (for example, acetone, cyclohexanone), nitriles (for example, acetonitrile, adiponitrile or benzonitrile), aromatics (for example, 25 toluene, benzene, or xylene), esters (for example, methyl valerate, caprolactone), Texanol[®] (Union Carbide), or dimethylformamide.

EXAMPLES

35

The following non-limiting examples further illustrate the invention. All percentages are on a mole basis, unless otherwise noted.

EXAMPLE 1
Synthesis of Ligand 1



Ligand 1

5 Isopropyl 2-hydroxyphenylacetate was prepared using
 the procedure described in *J. Amer. Chem. Soc.*, 70, 1948,
 1930. To a flask were added 10 g of 2-hydroxy
 phenylacetic acid, 99 mL of isopropanol and 9.9 mL of
 concentrated sulfuric acid. The mixture was refluxed for
 10 5.5 hrs, poured into 400 mL of ice and extracted with 3 x
 100 mL of ether. The organic layer was washed with 100
 mL of aqueous solution of sodium bicarbonate (saturated).
 The organic fraction was dried over sodium sulfate and
 the solvent removed by rotary evaporation. The residue
 15 was flash chromatographed on silica gel eluted with 10%
 ethyl acetate/hexane to give 9.227 g of the desired
 product as a white solid. ^1H NMR (300 MHz, δ , CDCl_3):
 7.16 (m, 1H), 7.08 (dd, 1H), 6.92 (dd, 1H), 6.80 (m, 1H),
 5.04 (septet, $J = 6.2$ Hz, 1H), 3.60 (s, 2H), 1.25 (d, 6.2
 20 Hz, 6H).

The above phenol (4.8 g) was dissolved in 100 mL
 diethyl ether, and cooled to -40°C in a nitrogen purged
 glove box. Triethylamine (3.0 g) was added, followed by
 the addition of 2.1 g of diethyl phosphoramidous

dichloride. Upon addition of diethyl phosphoramidous dichloride, a white precipitate formed. The reaction mixture was stirred at room temperature for one hour, then filtered over a pad of Celite® (filter aid 5 manufactured by Johns Manville Corp.). The filtrate was concentrated in vacuo to yield 5.8 g (96%) of the corresponding phosphorous amidite. ^{31}P NMR (toluene): 141.7 ppm.

The above phosphorous amidite (5.8 g) was dissolved 10 in 100 mL anhydrous ether and cooled to -40°C. To the stirring amidite solution was added 23 mL of pre-cooled 1M HCl solution in ether via an addition funnel. Upon addition, white precipitate formed. The mixture was stirred for 10 minutes, and cooled back to - 15 40°C for 2 hours. The resulting slurry was filtered over a pad of Celite®, and concentrated in vacuo to yield 5.1 g of the corresponding phosphorochloridite. ^{31}P NMR (toluene): 162.1 ppm.

The above phosphorochloridite (5.12 g, 11 mmol) was 20 dissolved in cold ether (30 mL) and cooled to -30°C. To this was added di-*o*-tolyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate (2g, 3.61 mmol) while stirring, followed by dropwise addition of triethylamine 25 solution (1.1g in 5 mL ether). After the addition, the mixture was stirred at room temperature for 15 minutes, then left standing at -30°C overnight to yield a white slurry. The product was filtered through a pad of neutral alumina, and the filtrate was concentrated in vacuo to give a waxy white solid. This solid was washed 30 with hexanes to yield 2.0 g of white powder. ^{31}P NMR (toluene): major resonance at 129.4 ppm, along with minor peaks at 127.1, 131.3 ppm.

EXAMPLE 1AHydroformylation of 3-Pentenenitrile with Ligand
1/Rhodium bis(carbonyl)acetylacetone

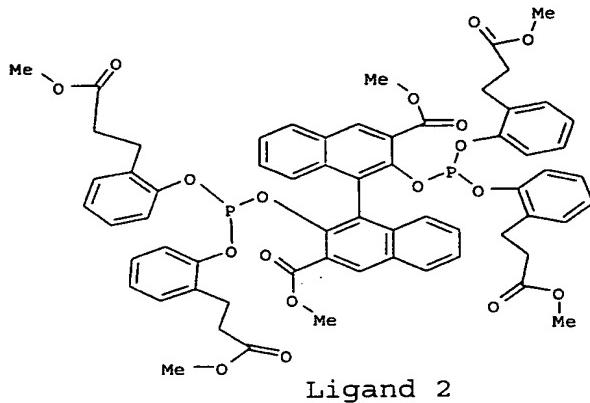
5 A solution containing 1.09 g of Ligand 1, 0.040 g of rhodium bis(carbonyl) acetylacetone, 2 g of ortho-dichlorobenzene (GC internal standard) and 70 g of 3-pentenenitrile was mixed and stirred with 3 g of Amberlyst® A-21 ion-exchange resin (weakly basic, 10 macroreticular resin available manufactured by Rohm and Haas) for 15 minutes. The resin was removed by filtration and the solution loaded into a 100 mL autoclave and heated with vigorous stirring under 0.45 MPa with a 1:1 mixture of CO and H₂ under flowing CO/H₂ at a rate of 20 15 mL/min at 95°C for 6 hours. A sample was removed from the reactor after 6 hours and analyzed by gas chromatography using an HP 5890A Chromatograph with a Quadrex 23 fused silica capillary column (30 meters, 0.32 mm I.D., 0.25 µm film thickness) purchased from the Quadrex Corporation.

20 GC analysis: (mole%):
2-pentenenitrile 2.13%, valeronitrile 8.1%, 3-pentenenitrile 8%, 5-formylvaleronitrile 70.2%.
Conversion is the percentage of 3- and 4-pentenenitrile which is converted to products.
25 Selectivity is the percentage of the product mixture that is comprised of 5-formylvaleronitrile, and linearity is the percentage the aldehyde products that is comprised of 5-formylvaleronitrile. Conversion of pentenenitriles: 92%; selectivity to 30 5-formylvaleronitrile: 78% on a mole basis; linearity of aldehydes produced: 87%.

EXAMPLE 1BHydroformylation of Methyl 3-Pentenoate with Ligand 1
/Rhodium bis(carbonyl)acetylacetone

5 In a drybox was prepared a solution containing methyl
3-pentenoate (0.5 M), rhodium bis(carbonyl)acetylacetone
(1.0 mM), and 1,2-dichlorobenzene (internal standard,
0.14 M) in toluene. A portion of this solution was added
to a glass-lined pressure vessel and enough of a solution
10 of the ligand (0.05 M) in toluene was added to give 4.6
equivalents of Ligand 1 to Rh. The reactor was sealed,
pressurized to 0.45 MPa with a 1:1 mixture of CO and H₂
and heated to 95°C for 3 hours. The reactor was cooled
and depressurized, and a sample of the reaction mixture
15 was analyzed by gas chromatography on an HP 5890A
Chromatograph with a DB-FFAP fused silica capillary
column (30 meters, 0.32 mm I.D., 0.25 um film thickness)
purchased from JW Scientific. GC analysis: (mole %)
methyl-2-pentenoate 5.6%, methyl valerate 1.7%, methyl-3-
20 pentenoate 28.3%, methyl-5-formylvalerate 62.2%.
Conversion of methyl pentenoates: 71%; selectivity to
methyl-5-formylvalerate: 88% on a mole basis; linearity
of aldehydes produced: 98%.

EXAMPLE 2
Synthesis of Ligand 2



5 The phosphorochloridite of methyl 3-(2-hydroxyphenyl)propionate was prepared from PCl₅ in toluene with triethylamine as base at -30°C. ³¹P NMR of the reaction mixture: 162.8 ppm. To this mixture was added dimethyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate and more triethylamine. The mixture was 10 filtered through Celite® and the solvent removed by rotary evaporation. The residue was dissolved in toluene and passed through basic alumina with toluene. The solvent was removed and the residue passed through silica gel with toluene and then tetrahydrofuran. Solvent was 15 removed from the tetrahydrofuran fraction and the residue vacuum dried. ³¹P {H} NMR (202.4 MHz, CDCl₃): major resonance at 131.0 ppm with minor other resonances at 147.0 and 131.4 ppm.

20

EXAMPLE 2A
Hydroformylation of 3-Pentenenitrile with Ligand 2
/Rhodium bis(carbonyl)acetylacetone

25 A solution containing 0.018 g of rhodium bis(carbonyl)acetylacetone, 3.7 equivalents of Ligand 2 to Rh, 1 g of ortho-dichlorobenzene and 30 g of 3-pentenenitrile was loaded into a 100 mL autoclave and

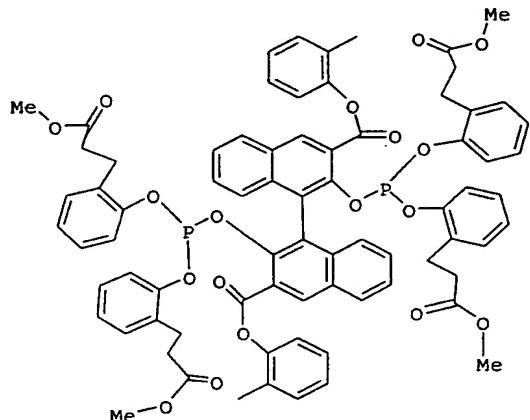
heated with vigorous stirring under 0.45 MPa with a 1:1 mixture of CO and H₂ while flowing CO/H₂ at a rate of approximately 30 mL/min at 95°C for 5 hours. The reactor was cooled and depressurized, and a sample of the
5 reaction mixture was analyzed by gas chromatography on an HP 5890A Chromatograph with a Quadrex 23 fused silica capillary column (30 meters, 0.32 mm I.D., 0.25 um film thickness) purchased from the Quadrex Corporation. GC analysis: (mole %) 2-pentenenitrile 3.6%, valeronitrile 10 5.4 %, 3-pentenenitrile 7.5%, 5-formylvaleronitrile 53.5%. Conversion of pentenenitriles: 92%; selectivity to 5-formylvaleronitrile: 58% on a mole basis; linearity of aldehydes produced: 73%.

15

EXAMPLE 2BHydroformylation of Methyl 3-Pentenoate with Ligand
2/Rhodium bis(carbonyl)acetylacetone

Reaction was run as in example 1B, but with 4.6
20 equivalents of Ligand 2 to Rh. GC analysis: (mole %) methyl-2-pentenoate 6.4%, methyl valerate 3.2%, methyl-3-pentenoate 21.2%, methyl 5-formylvalerate 66.4%. Conversion of methyl pentenoates: 79%; selectivity to methyl 5-formylvalerate: 84% on a mole basis; linearity
25 of aldehydes produced: 96%.

EXAMPLE 3
Synthesis of Ligand 3



Ligand 3

5

The same procedure as example 2 was followed, but with di-*o*-tolyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate instead of dimethyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate. ^{31}P {H} nmr (202.4 MHz, CDCl_3): major resonance at 129.4 ppm with minor resonances at 148.3 and 131.4 ppm

EXAMPLE 3A

Hydroformylation of 3-Pentenenitrile with Ligand 3

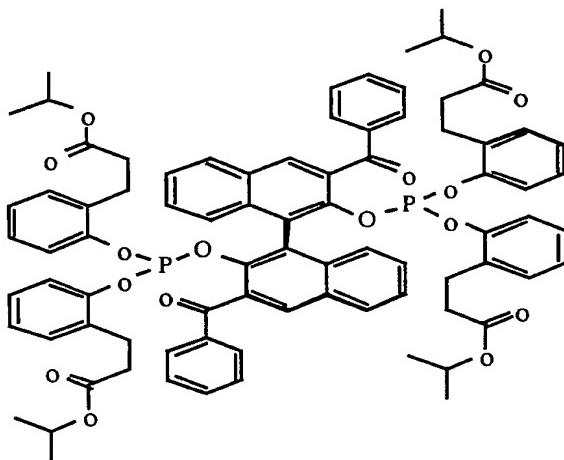
15 /Rhodium bis(carbonyl)acetylacetone

Reaction was run as in example 2A, but with 3.7 equivalents of Ligand 3 to Rh for 5 hours. GC analysis: (mole%) 2-pentenenitrile 1.8%, valeronitrile 19.0%, 3-pentenenitrile 4.0%, 5-formylvaleronitrile 60.5%. Conversion of pentenenitriles: 96%; selectivity to 5-formylvaleronitrile: 63% on a mole basis; linearity of aldehydes produced: 81%.

EXAMPLE 3B

Hydroformylation of Methyl-3-Pentenoate with Ligand 3
/Rhodium bis(carbonyl)acetylacetonate

5 Reaction was run as in example 1B, but with 4.6 equivalents of Ligand 3 to Rh. GC analysis: (mole %) methyl 2-pentenoate 4.3%, methyl valerate 1.5%, methyl 3-pentenoate 36.9%, methyl 5-formylvalerate 54.5%. Conversion of methyl pentenoates: 62%; selectivity to
10 methyl 5-formylvalerate: 88% on a mole basis; linearity of aldehydes produced: 96%.

EXAMPLE 4
Synthesis of Ligand 4

15

Ligand 4

With stirring under dry nitrogen, 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylic acid (8.42 g, 22.5 mmol) was dissolved in dry tetrahydrofuran (500 mL) then cooled to -78°C with a dry ice/acetone bath.
20 Phenyllithium (100 mL of 1.8 M in 70/30 cyclohexane/ether, 0.18 mol) was added dropwise, then the solution was allowed to warm to ambient temperature. After stirring overnight, deionized water (50 mL) was slowly added to the reaction solution at 0°C. With
25 vigorous stirring, 1 M hydrochloric acid was added

dropwise until the water phase became strongly acidic (pH = 2). The organic phase was washed with water in a separatory funnel, then dried over magnesium sulfate and evaporated. The orange residue was redissolved in dichloromethane and eluted through a silica gel plug. The orange filtrate was evaporated to yield 2,2'-dihydroxy-1,1'-binaphthalene-3,3'-bis(phenylketone) as a yellow solid (10.5 gm).

The phosphorochloridite of isopropyl 3-(2-hydroxyphenyl)priopionate was prepared as described in example 1. ^{31}P NMR (toluene) : δ 163. 2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-bis(phenylketone) was added to the phosphorochloridite of isopropyl 3-(2-hydroxyphenyl)priopionate in the presence of triethylamine, following the procedure outlined in example 1 to yield Ligand 4. ^{31}P NMR (toluene) : δ 127 (major), 123 (minor).

EXAMPLE 4A

Hydroformylation of 3-Pentenenitrile with Ligand 4
/Rhodium bis(carbonyl)acetylacetonate

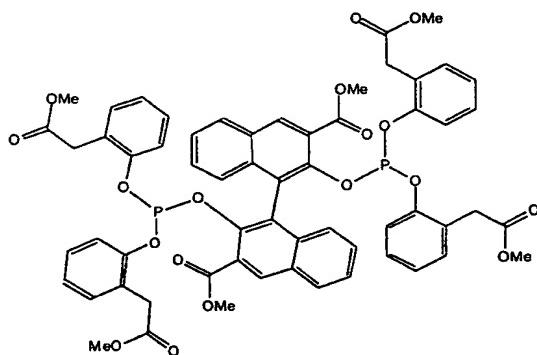
In a drybox was prepared a solution containing 3-pentenenitrile (0.5 M), rhodium bis(carbonyl)acetylacetonate (0.85 mM), and 1,2-dichlorobenzene (internal standard, 0.14 M) in toluene. A portion of this solution was added to a glass-lined pressure vessel and enough of a solution of the ligand (0.05 M) in toluene was added to give 2.9 equivalents of Ligand 4 to Rh. The reactor was sealed, pressurized to 0.45 MPa with a 1:1 mixture of CO and H₂ and heated to 95°C for 3 hours. The reactor was cooled and depressurized, and a sample of the reaction mixture was analyzed by gas chromatography on an HP 5890A Gas Chromatograph with a Quadrex 23 fused silica capillary column (30 meters, 0.32 mm I.D., 0.25 um film thickness) purchased from the Quadrex Corporation. GC analysis: (mole%) 2-pentenenitrile 7.2%, valeronitrile 9.9%, 3-

pentenenitrile 24.7%, 5-formylvaleronitrile 53.6%.

Conversion of pentenenitriles: 78%; selectivity to 5-formylvaleronitrile: 72% on a mole basis; linearity of aldehydes produced: 90%.

5

EXAMPLE 5
Synthesis of Ligand 5



Ligand 5

10

The reaction was carried out in an inert atmosphere. In a 100 mL flask was added 0.206 g of phosphorus trichloride and 16 g of toluene. The mixture was cooled to -30°C and 0.499 g of methyl 2-hydroxyphenyl acetate was added. To this cooled solution was added dropwise 0.400 g of triethylamine in 8 g of toluene which had been cooled to -30°C. After addition of the triethylamine, 0.605 g of dimethyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate was added along with 0.300 g of triethylamine. The mixture was stirred overnight, filtered over Celite® (Johns Manville Corp.), and solvent removed by rotary evaporation. A thick yellow oil (1.274 g) was obtained. ^{31}P {H} NMR (202.4 MHz, CDCl_3) indicated a mixture: 145.8, 130.9, 130.4, 129.4, 129.0 ppm. Matrix Assisted Laser Desorption Ionization Mass Spectroscopy (MALDI MS): found $M^+ + \text{Na}:$ 1144.5; calculated for $\text{C}_{60}\text{H}_{52}\text{O}_{18}\text{P}_2 + \text{Na}:$ 1145.2

EXAMPLE 5AHydroformylation of 3-Pentenenitrile with Ligand
5/Rhodium bis(carbonyl)acetylacetone

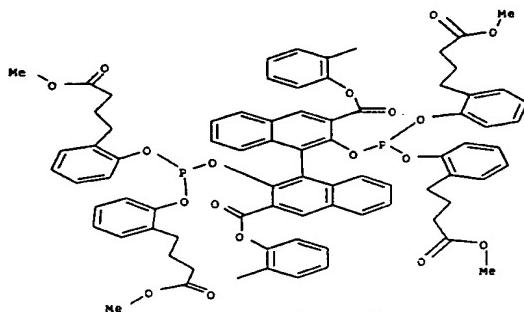
5 Reaction was run as in example 4A, but with 5.4 equivalents of Ligand 5 to Rh. GC analysis: (mole %) 2-pentenenitrile 5.6%, valeronitrile 7.9%, 3-pentenenitrile 21.7%, 5-formylvaleronitrile 61.7%. Conversion of pentenenitriles: 86%; selectivity to 5-formylvaleronitrile: 79% on a mole basis; linearity of aldehydes produced: 95%.

10

EXAMPLE 5BHydroformylation of Methyl-3-Pentenoate with Ligand
5/Rhodium bis(carbonyl)acetylacetone

15 Reaction was run as in example 1B, but with 4.6 equivalents of Ligand 5 to Rh. GC analysis: (mole %) methyl 2-pentenoate 6.8%, methyl valerate 3.4%, methyl 3-pentenoate 17.4%, methyl 5-formylvalerate 70.1%. Conversion of methyl pentenoates: 82%; selectivity to methyl 5-formylvalerate: 85% on a mole basis; linearity of aldehydes produced: 97%.

20

EXAMPLE 6Synthesis of Ligand 6

Ligand 6

25 4-(2-Hydroxyphenyl)butyric acid (1g, 5.55 mmol) was dissolved in 20 mL anhydrous methanol, and 5 mL sulfuric acid. The mixture was heated to reflux for 6 hours.

After aqueous workup, 1.14 g of methyl 4-(2-hydroxyphenyl)butyrate was obtained. ^1H NMR (CDCl_3): 1.92 (q, 2H), 2.40 (t, 2H), 2.65 (t, 2H), 3.72 (s, 3H), 6.84 (m, 2H), 7.10 (m, 2H).

5 Methyl 4-(2-Hydroxyphenyl)butyrate was reacted with diethylphosphoramidous dichloride as described for example 1, to give the corresponding phosphorous amidite. ^{31}P NMR (toluene): 142 ppm. The resulting phosphorous amidite was treated with 1M HCl as described for example 10 1, to yield the corresponding phosphochloridite. ^{31}P NMR (toluene): 162 ppm. The phosphochloridite was then reacted with di-o-tolyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate in the same manner as described for example 1, to yield ligand 6. NMR indicated 15 a mixture. ^{31}P NMR (toluene): 130.7, 131.2, 131.8; resonances were about the same intensity.

EXAMPLE 6A

Hydroformylation of 3-Pentenenitrile with Ligand 6 /Rhodium bis(carbonyl)acetylacetone

20 Reaction was run as in example 4A, but with 2.9 equivalents of Ligand 6 to Rh. GC analysis: (mole%) 2-pentenenitrile 2.6%, valeronitrile 10.0%, 3-pentenenitrile 26.3%, 5-formylvaleronitrile 49.6%.
25 Conversion of pentenenitriles: 74%; selectivity to 5-formylvaleronitrile: 68% on a mole basis; linearity of aldehydes produced: 82%.

EXAMPLE 6B

Hydroformylation of Methyl 3-pentenoate with Ligand 6/Rhodium bis(carbonyl)acetylacetone

30 Reaction was run as in example 1B, but with 4.6 equivalents of Ligand 6 to Rh. GC analysis: (mole %) 35 methyl 2-pentenoate 4.6%, methyl valerate 1.7%, methyl-3-pentenoate 49.5%, methyl 5-formylvalerate 41.8%. Conversion of methyl pentenoates: 49%; selectivity to

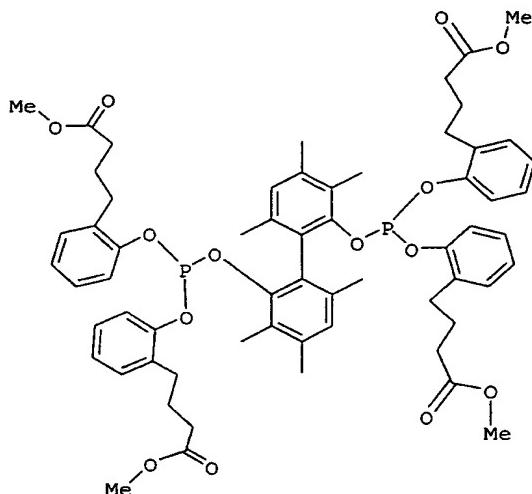
methyl 5-formylvalerate: 85% on a mole basis; linearity of aldehydes produced: 98%.

EXAMPLE 6C

5 Hydroformylation of Undecene with Ligand 6/Rhodium bis(carbonyl)acetylacetone

In a drybox was prepared a solution containing undecene (0.5 M), rhodium bis(carbonyl)acetylacetone (0.85 mM), and 1,2-dichlorobenzene (internal standard, 0.14 M) in toluene. A portion of this solution was added to a glass-lined pressure vessel and enough of a solution of the ligand (0.05 M) in toluene was added to give 5.5 equivalents of Ligand 6 to Rh. The reactor was sealed, 10 pressurized to 0.45 MPa with a 1:1 mixture of CO and H₂ and heated to 95°C for 3 hours. The reactor was cooled and depressurized, and a sample of the reaction mixture was analyzed by gas chromatography on an HP 5890A Gas Chromatograph with a DB-Wax fused silica capillary column (30 meters, 0.32 mm I.D., 0.25 um film thickness) purchased from J&W Scientific Company. GC analysis: (mole %) undecane (1.8%), 1-undecene (3.7%), internal undecenes (52.8%), methylundecanal (0.2%), dodecanal (41.4%). Conversion of 15 undecenes: 58%; selectivity to dodecanal: 97% on a mole basis; linearity of aldehydes produced: 99.5%.
20
25

EXAMPLE 7
Synthesis of Ligand 7



Ligand 7

Methyl 4-(2-Hydroxyphenyl)butyrate was converted to the corresponding phosphorochloridite as described for example 6. The phosphochloridite was reacted with 3,3',4,4',6,6'-hexamethyl-2,2'-biphenol, following the procedure described for example 1, to give ligand 7. NMR indicated a mixture. ^{31}P NMR (toluene): 131, 136, 137; resonances were about the same intensity.

EXAMPLE 7A

5 Hydroformylation of 3-Pentenenitrile with Ligand 7
/Rhodium bis(carbonyl)acetylacetone

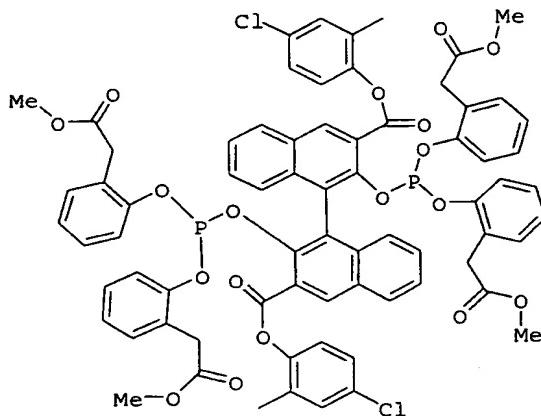
Reaction was run as in example 4A, but with 5.7 equivalents of Ligand 7 to Rh. GC analysis: (mole%)
10 2-pentenenitrile 2.2%, valeronitrile 10.0%,
3-pentenenitrile 35.4%, 5-formylvaleronitrile 36.6%.
Conversion of pentenenitriles: 64%; selectivity to
5-formylvaleronitrile: 57% on a mole basis; linearity of
aldehydes produced: 70%.

EXAMPLE 7B

Hydroformylation of Methyl 3-pentenoate with Ligand
7/Rhodium bis(carbonyl)acetylacetone

5 Reaction was run as in example 1B, but with 4.6 equivalents of Ligand 7 to Rh. Conversion of methyl pentenoates: 65%; selectivity to methyl 5-formylvalerate: 65% on a mole basis; linearity of aldehydes produced: 93%.

10

EXAMPLE 8Synthesis of Ligand 8

Ligand 8

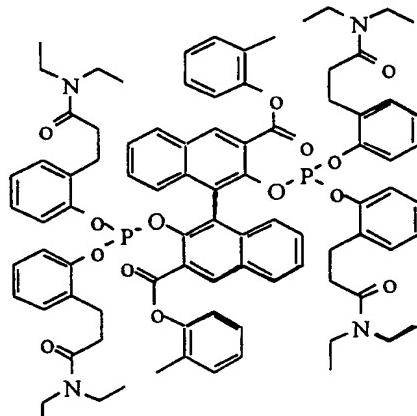
15 Methyl 2-hydroxyphenyl acetate was reacted with diethylphosphoramidous dichloride as described in example 1, to yield the corresponding phosphorous amidite. ³¹P NMR (toluene): 137 ppm. The phosphorous amidite was treated with 1M HCl solution as described in example 1, 20 to yield the corresponding phosphorochloridite. ³¹P NMR (toluene): 158 ppm. The chloridite was then reacted with bis(4-chloro-2-methylphenyl)-2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate as described in example 1, to yield Ligand 8. ³¹P NMR (toluene): 127 (major), 25 128, 131.

EXAMPLE 8A

Hydroformylation of 3-Pentenenitrile with Ligand 8
/Rhodium bis(carbonyl)acetylacetone

- 5 Reaction was run as in example 4A, but with 5.5 equivalents of Ligand 8 to Rh. GC analysis: (mole%) 2-pentenenitrile 2.3%, valeronitrile 8.1%, 3-pentenenitrile 13.5%, 5-formylvaleronitrile 69.8%. Conversion of pentenenitriles: 86%; selectivity to
- 10 5-formylvaleronitrile: 81% on a mole basis; linearity of aldehydes produced: 92%.

EXAMPLE 9

Synthesis of Ligand 9

Ligand 9

Diethylamine (98.5 g) and dihydrocoumarin (20.0 g) were refluxed for 4 hours. Excess diethylamine was removed in vacuo to leave 34.0 g of N,N-diethyl-3-(2-hydroxyphenyl) propionamide. ¹H NMR (CDCl₃): 7.26-7.03 (m, 2H), 6.91 (dd, 1H), 6.81 (td, 1H), 3.37 (quartet, 2H), 3.26 (quartet, 2H), 2.95 (m, 2H), 2.71 (m, 2H), 1.10 (quartet, 6H).

In a nitrogen purged glove box, N,N-diethyl-3-(2-hydroxyphenyl) propionamide (5.0 g) was dissolved in 110 mL anhydrous THF (tetrahydrofuran), and cooled to -30°C. To this was added diethylphosphoramidous dichloride (1.97

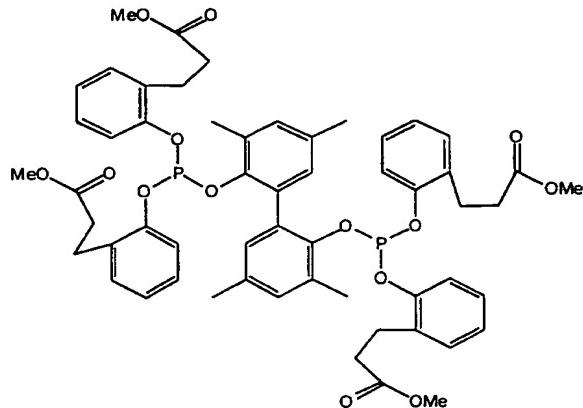
g), followed by dropwise addition of triethylamine (2.97 g). The mixture was stirred at room temperature for 10 minutes, then kept at -30°C for 2 hours. The resulting white slurry was filtered over a pad of Celite®, concentrated to yield 6.1 g of the corresponding phosphorous amidite. ^{31}P NMR (toluene): 141.5 ppm. The above phosphorous amidite (2.5 g) was dissolved in 55 mL anhydrous ether and cooled to -40°C. To the stirring amidite solution was added 11 mL of pre-cooled 1M HCl solution in ether via an addition funnel. Upon addition, white precipitate formed. The mixture was stirred for 10 minutes, and cooled back to -40°C for 1 hours. The resulting slurry was filtered over a pad of Celite®, and concentrated in vacuo to yield 3.1 g of the corresponding phosphorochloridite. ^{31}P NMR (toluene): 157.9 ppm. The chloridite was then reacted with di-*o*-tolyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate as described in example 1, to yield Ligand 9. ^{31}P NMR (toluene): 132 (major), 134 (minor), 148 (minor).

EXAMPLE 9A

Hydroformylation of 3-Pentenenitrile with Ligand 9 /Rhodium bis(carbonyl)acetylacetonate

- 5 Reaction was run as in example 4A, but with 10 equivalents of Ligand 9 to Rh. GC analysis: (mole%) 2-pentenenitrile 1.2%, valeronitrile 7.9%, 3-pentenenitrile 21.3%, 5-formylvaleronitrile 57.4%. Conversion of pentenenitriles: 76%; selectivity to
- 10 5-formylvaleronitrile: 75% on a mole basis; linearity of aldehydes produced: 86%.

EXAMPLE 10
Synthesis of Ligand 10



Ligand 10

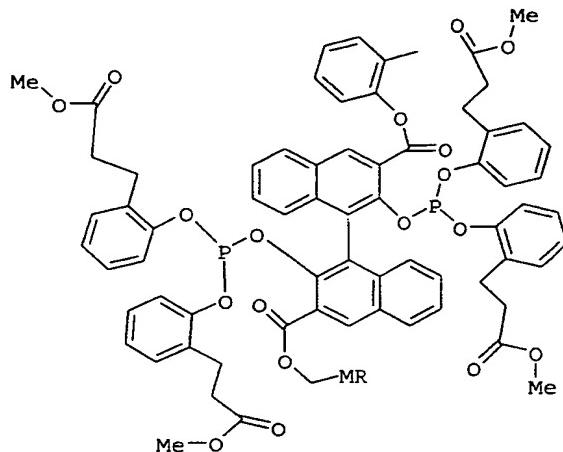
5 The procedure of example 2 was followed, except
 3,3',5,5'-tetramethyl-2,2'-biphenol was used instead of
 dimethyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-
 dicarboxylate. ^{31}P {H} NMR (202.4 MHz, CDCl_3): major
 resonance at 133.4 ppm with minor resonances at 141.9,
 10 133.6, 130.6 ppm.

EXAMPLE 10A

Hydroformylation of Methyl 3-Pentenoate with Ligand 10
/Rhodium bis(carbonyl)acetylacetone

15 Reaction was run as in example 1B, but with 4.6
 equivalents of Ligand 10 to Rh. GC analysis: (mole %)
 methyl 2-pentenoate 6.8%, methyl valerate 3.3%, methyl 3-
 pentenoate 44.4%, methyl 5-formylvalerate 42.4%.
 Conversion of methyl pentenoates: 55%; selectivity to
 20 methyl 5-formylvalerate: 78% on a mole basis; linearity
 of aldehydes produced: 95%.

EXAMPLE 11
Synthesis of Ligand 11



5

Ligand 11

"MR" denotes Merrifield's resin. 0.757 g (0.6 mmol) of the polymer supported diol prepared by partial esterification of 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylic acid with Merrifield's resin, followed by esterification with *o*-cresol, was placed in 15 mL of anhydrous toluene, followed by 0.983 g of ClP[OC₆H₄-2-(CH₂)₂CO₂CH₃]₂ (2.4 mmol) and 0.465 g of diisopropylethylamine (3.6 mmol). After shaking overnight, the resin changed from orange to light yellow. The supported ligand was collected by filtration and washed with toluene (20 mL), tetrahydrofuran (20 mL), and CH₂Cl₂ (20 mL) before drying under vacuum; Elemental analysis: 1.74 - 1.97 wt % P; IR (KBr): 1736 cm⁻¹ (vs).

20 A portion of the supported ligand was treated with excess Ni(COD)₂, followed by about 0.1 MPa of carbon monoxide to give the supported complex P₂Ni(CO)₂ (P₂ denotes the supported ligand). The infrared spectrum of this material shows, in addition to an ester band at 1730 cm⁻¹, strong bands at 2045 and 1996 cm⁻¹, consistent with formation of the desired dicarbonyl species. A very weak band at 2084 cm⁻¹ indicates formation of a trace amount of

a supported PNi(CO)₃ species, where P denotes a supported monophosphite ligand.

EXAMPLE 11A

5 Hydroformylation of 3-Pentenenitrile with Ligand 11
 /Rhodium bis(carbonyl)acetylacetone

In a drybox was prepared a solution containing 3-pentenenitrile (0.5 M), rhodium bis(carbonyl)acetylacetone (0.85 mM), and 1,2-dichlorobenzene (internal standard, 0.14 M) in toluene. A portion of this solution was added to a glass-lined pressure vessel containing 5.3 molar equivalents of Ligand 11 to Rh. The reactor was sealed, 10 pressurized to between 0.45 MPa with a 1:1 mixture of CO and H₂ and heated to between 95°C for 3 hours. The reactor was cooled and depressurized, and a sample of the reaction mixture was analyzed by gas chromatography on an HP 5890A Chromatograph with a Quadrex 23 fused silica 15 capillary column (30 meters, 0.32 mm I.D., 0.25 um film thickness) purchased from the Quadrex Corporation. GC analysis: GC analysis: (mole%) 2-pentenenitrile 4.7%, 20 valeronitrile 13.6%, 3-pentenenitrile 23.3%, 5-formylvaleronitrile 46.3%. 25 Conversion of pentenenitriles: 77%; selectivity to 5-formylvaleronitrile: 60% on a mole basis; linearity of aldehydes produced: 79%.

EXAMPLE 11B

30 Hydroformylation of Methyl 3-Pentenoate with Ligand 11
 /Rhodium bis(carbonyl)acetylacetone

In a drybox was prepared a solution containing methyl-3-pentenoate (0.5 M), rhodium bis(carbonyl)acetylacetone (1.0 mM), and 35 1,2-dichlorobenzene (internal standard, 0.14 M) in toluene. A portion of this solution was added to a glass-lined pressure vessel containing 4.9 molar

equivalents of Ligand 11 to Rh. The reactor was sealed, pressurized to 0.45 MPa with a 1:1 mixture of CO and H₂ and heated to 95°C for 3 hours. The reactor was cooled and depressurized, and a sample of the reaction mixture was
5 analyzed by gas chromatography on an HP 5890A Chromatograph with a DB-FFAP fused silica capillary column (30 meters, 0.32 mm I.D., 0.25 um film thickness) purchased from JW Scientific. GC analysis: (mole %) methyl-2-pentenoate 2.7%, methyl valerate 0.8%, methyl-3-
10 pentenoate 75.3%, methyl 5-formylvalerate 19.1%. Conversion of methyl pentenoates: 24%; selectivity to methyl 5-formylvalerate: 79% on a mole basis; linearity of aldehydes produced: 93%.

15 EXAMPLES 12, 13, 14

Synthesis of Ligands 12, 13, and 14

Ligands 12, 13, and 14 were prepared as described for Ligand 11 in example 11. Characterization data is
20 provided in Table 1. ~~MR~~ in the structures below refers to Merrifield's resin.

Table 1. Characterization Data for polymer-bound ligands

Example	Ligand	Structure	Elemental Analysis (wt % P)	IR (KBr, cm ⁻¹)
12	12		2.03	1736 (vs)
13	13		1.76	1734 (vs)
14	14		1.80	1734 (vs)

EXAMPLES 12A-14A

5

Reactions were run as in example 11A. The results are summarized in Table 2, in which CONV (conversion) is the percentage of 3 and 4 pentenenitrile which is converted to products, SEL (selectivity) is the percentage of the product mixture that is comprised of 5-formylvaleronitrile, and LIN (linearity) is the percentage the aldehyde products that is comprised of 5-formylvaleronitrile.

Table 2. 3-Pentenenitrile Hydroformylation Results for polymer-bound ligands

Example	Ligand	CONV	SEL	LIN
12A	12	65.5	64.2	77.3
13A	13	64.7	59.2	71.9
14A	14	86.7	57.6	73.8

5

EXAMPLES 12B-14B

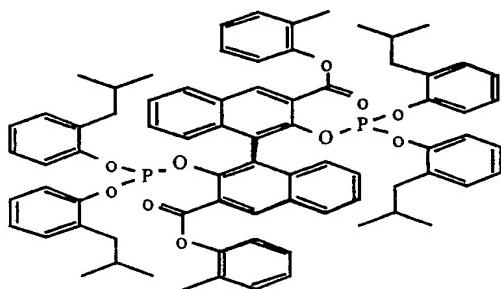
The ligands were prepared as above. Reactions using methyl 3-pentenoate as reactant were run as in Example 10 11B. Results are in Table 3.

Table 3. Methyl 3-Pentenoate Hydroformylation Results

Example	Ligand	CONV	SEL	LIN
12B	12	54.8	81.2	93.3
13B	13	68.9	82.5	93.4
14B	14	55.4	80.3	92.0

15

COMPARATIVE EXAMPLE 1
Synthesis of Ligand 15



Ligand 15

2-Hydroxy-isobutyrophenone was prepared from phenol following the procedure described in *Canadian Journal of Chemistry*, 31, 1956, 851. To a solution of 2-hydroxy-isobutyrophenone (2g, 12.2 mmol) in trifluoroacetic acid (14 g, 122 mmol) was slowly added triethylsilane (26.8 mmol). The solution was stirred at room temperature for 6 hours. Saturated sodium bicarbonate solution was added to the reaction mixture, followed by ether. The layers were separated, and the aqueous layer was extracted with ether. The organic layers were combined, dried over magnesium sulfate, and concentrated. The crude material was distilled under vacuum (about 9.3×10^{-4} MPa, 75°C). The distillate was washed with potassium hydroxide solution, followed by addition of hydrogen chloride solution, and extraction with ether. The ether layers were combined, dried over magnesium sulfate, and concentrated to give 1.0 g (55%) of 2-isobutylphenol. ¹H NMR (300 Mhz, δ, CDCl₃): 7.0 (m, 2H), 6.8 (t, 1H), 6.7 (d, 1H), 4.6 (br. s, 1H), 2.4 (d, 2H), 1.9 (s, 1H), 0.9 (d, 6H).

The above phenol (0.78 g) was dissolved in 25 mL diethyl ether, and cooled to -40°C in a nitrogen purged glove box. Triethylamine (0.68 g) was added, followed by the addition of 0.45 g of diethylphosphoramidous dichloride. Upon addition of diethylphosphoramidous dichloride, a white precipitate formed. The reaction mixture was stirred at room temperature for one hour, then filtered over a pad of Celite®. The filtrate was concentrated in vacuo to yield 1.0 g (97%) of the corresponding phosphorous amidite. ³¹P NMR(toluene): 136 ppm. The above phosphorous amidite (1.0 g) was dissolved in 25 mL anhydrous ether and cooled to -40°C. To the stirring amidite solution was slowly added 5.0 mL of pre-cooled 1M HCl solution in ether. Upon addition, white precipitate formed. The mixture was stirred for 10 minutes, and cooled back to -40°C for 2 hours. The resulting slurry was filtered over a pad of Celite®, and

concentrated in vacuo to yield 0.85 g of the corresponding phosphorochloridite. ^{31}P NMR (toluene): 161 ppm.

The above phosphorochloridite was reacted with di-o-
5 tolyl 2,2'-dihydroxyl-1,1'-binaphthalene-3,3'-dicarboxylate and triethylamine in the same manner as described for example 1 to yield Ligand 15. ^{31}P NMR (toluene): 129.9 ppm.

10

COMPARATIVE EXAMPLE 1AHydroformylation of 3-Pentenenitrile with Ligand 15/
Rhodium bis(carbonyl)acetylacetone

Reaction was run as in example 4A, but with Ligand
15 15. Conversion of 3-pentenenitrile: 73%; selectivity to 5-formylvaleronitrile: 64% on a mole basis; linearity of aldehydes produced: 73%.

20

COMPARATIVE EXAMPLE 1BHydroformylation of Methyl 3-Pentenoate with Ligand 15/
Rhodium bis(carbonyl)acetylacetone

Reaction was run as in example 1B, but with 4.6 equivalents of Ligand 15 to Rh. GC analysis: (mole %) methyl 2-pentenoate 5.5%, methyl valerate 1.5%, methyl 3-pentenoate 46.7%, methyl 5-formylvalerate 43.3%. Conversion of pentenenitriles: 83%; selectivity to methyl 5-formylvalerate: 78% on a mole basis; linearity of aldehydes produced: 96%.

30

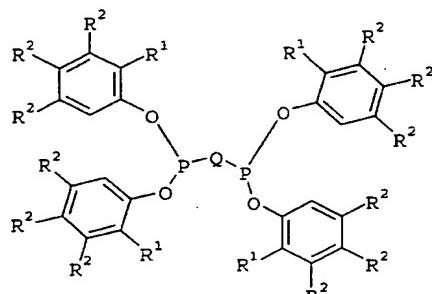
In contrast to the prior art, multidentate phosphite ligands of the present invention in which at least one R¹ group is R³Z provide high selectivities in the hydroformylation of 3-pentenenitrile. A comparison of the performance of comparative example Ligand 15 with that of sterically similar Ligand 1 (a ligand of the present invention) shows that the selectivity in 3-pentenenitrile hydroformylation is 14% higher for

Ligand 1. Similarly, Ligand 1 performed better in methyl-3-pentenoate hydroformylation than the sterically analogous comparative example Ligand 15, leading to 10% higher selectivity of 5-formylvalerate.

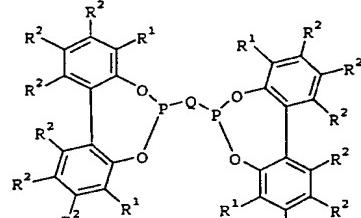
WHAT IS CLAIMED:

1. A process for converting a C₂ to C₂₀ acyclic monoethylenically unsaturated compound to its corresponding terminal aldehyde, comprising reacting the compound with CO and H₂ in the presence of a Group VIII transition metal and at least one multidentate phosphite ligand of the formulae I, II or III:

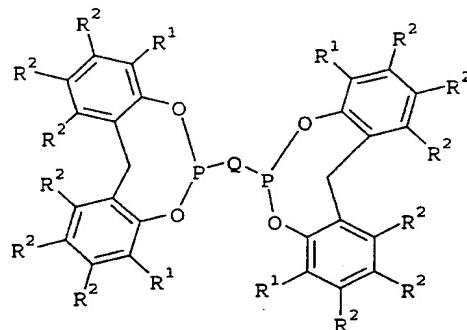
10



I



II



III

15

wherein:

each R¹ independently is C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, F, Cl, -CO₂R⁴, -OR⁴, or -R³Z, provided that at 20 least one R¹ is -R³Z;

each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;

each R³ independently is C₁ to C₁₀ alkylene;

5 each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;

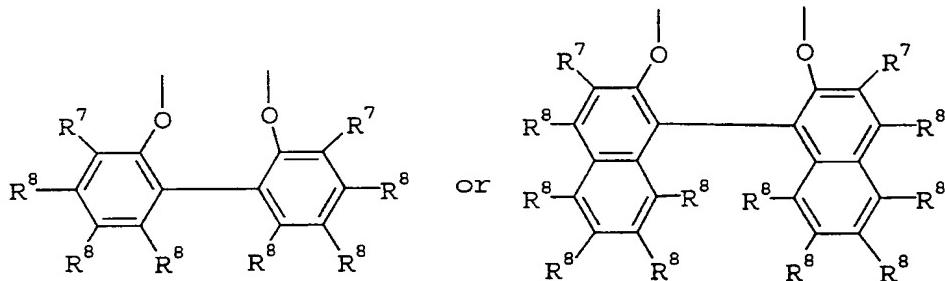
each Z is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)SR⁴, -SR⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶,

10 ~~C(R⁵)=NR⁶~~, -C(R⁵)=N-O-R⁶, -P(O)(OR⁴)(OR⁴), -S(O)₂R⁴, -S(O)R⁴, -C(O)OC(O)R⁴, -NR⁴CO₂R⁴, -NR⁴C(O)NR⁵R⁶, or -CN;

each R⁵ independently is H, C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;

15 each R⁶ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;

Q is a divalent bridging group of the formula:



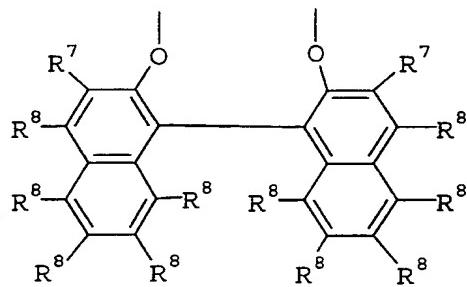
20

wherein:

each R⁷ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, -CF₃, -C(R⁵)=NR⁶, -NR⁵R⁶ or -R³Z; and

25 each R⁸ is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or CF₃.

2. The process of claim 1 in which the ligand is of formula I wherein:
- each R¹ independently is -R³Z;
- each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;
- each R³ independently is C₁ to C₄ alkylene;
- each Z independently is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, or -C(R⁵)=NR⁶;
- Q is a divalent bridging group of the formula:



each R⁷ independently is -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, or -C(R⁵)=N(R⁶); and

each R⁸ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

3. The process of claim 2 in which each R² is H; each R³ is C₁ to C₃ alkylene; and each Z is -CO₂R⁴.
4. The process of claim 3 in which the Group VIII transition metal is selected from the group consisting of rhodium, cobalt, iridium, palladium, and platinum.
5. The process of claim 4 in which the metal is rhodium.
6. The process of claim 5 in which the rhodium is added in the form of a rhodium hydride, halide, organic

acid salt, acetylacetone, inorganic acid salt, oxide, carbonyl compound, or amine compound.

7. The process of claim 6 in which the rhodium is added
5 in the form of rhodium bis(carbonyl)ketonate.

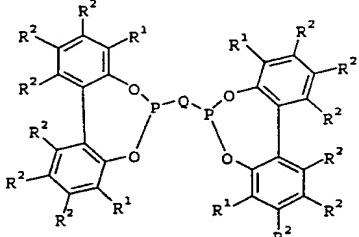
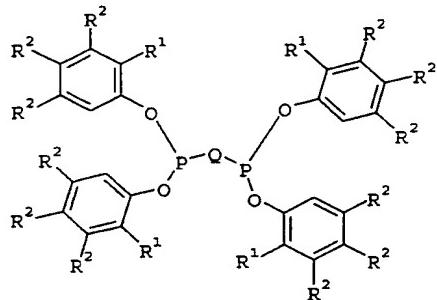
8. The process of claim 7 in which the acyclic
monoethylenically unsaturated compound is
3-pentenenitrile, 3-pentenoic acid, alkyl
10 3-pentenoate, or 3-pentenal.

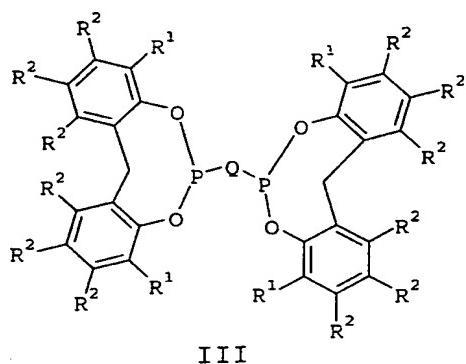
9. The process of claim 8 in which the ligand is on a
support.

15 10. The process of claim 9 in which the support is
polystyrene resin.

11. A multidentate phosphite ligand of the formulae I, II
or III:

20

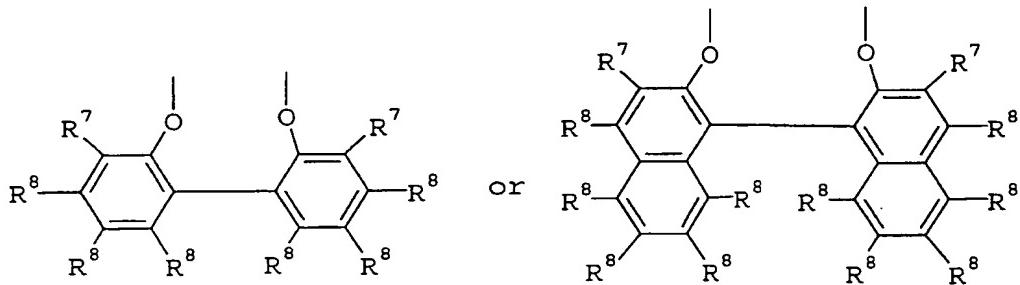




wherein:

- each R¹ independently is C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, F, Cl, -CO₂R⁴, -OR⁴, or -R³Z, provided that at least one R¹ is -R³Z;
- each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;
- each R³ independently is C₁ to C₁₀ alkylene;
- each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;
- each Z is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)SR⁴, -SR⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, 15 ~~NC(R⁵)=NR⁶~~, -C(R⁵)=N-O-R⁶, -P(=O)(OR⁴)(OR⁴), -S(O)₂R⁴, -S(O)R⁴, -C(O)OC(O)R⁴, -NR⁴CO₂R⁴, -NR⁴C(O)NR⁵R⁶, or -CN;
- each R⁵ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;
- each R⁶ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;

Q is a divalent bridging group of the formula:

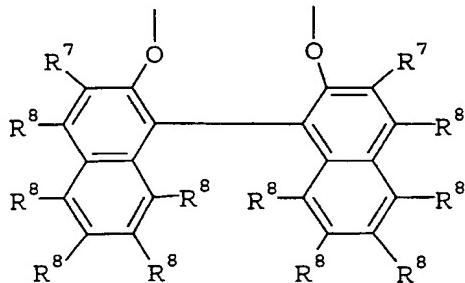


wherein:

- 5 each R⁷ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, -CF₃, -C(R⁵)=NR⁶, -NR⁵R⁶ or -R³Z; and
each R⁸ is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

- 10 12. The multidentate phosphite ligand of claim 11 in which the ligand is of formula I wherein:
each R¹ independently is -R³Z;
each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;
each R³ independently is C₁ to C₄ alkylene;
each Z independently is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, or -C(R⁵)=NR⁶

- 15 20 Q is a divalent bridging group of the formula:



wherein:

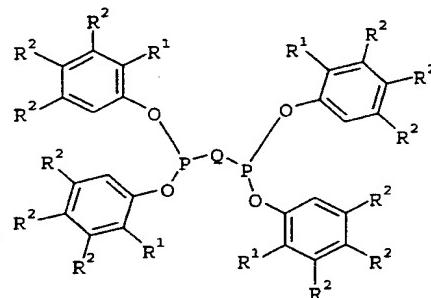
each R⁷ independently is -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, or -C(R⁵)=N(R⁶); and
 each R⁸ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

5

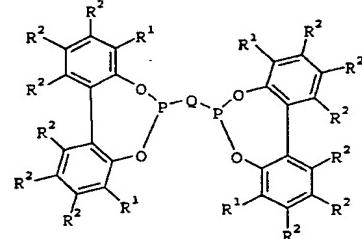
13. The multidentate phosphite ligand of claim 12 in which each R² is H; each R³ is C₁ to C₃ alkylene; each Z is -CO₂R⁴.

10

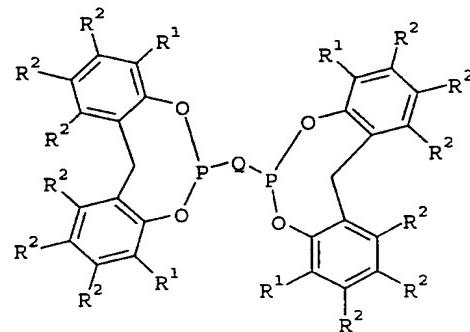
14. A catalyst comprising a Group VIII transition metal and a multidentate phosphite ligand selected from the group represented by the formulae I, II or III:



I



II



III

wherein:

each R¹ independently is C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, F, Cl, -CO₂R⁴, -OR⁴, or -R³Z, provided that at least one R¹ is -R³Z;

5 each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;

each R³ independently is C₁ to C₁₀ alkylene;

10 each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;

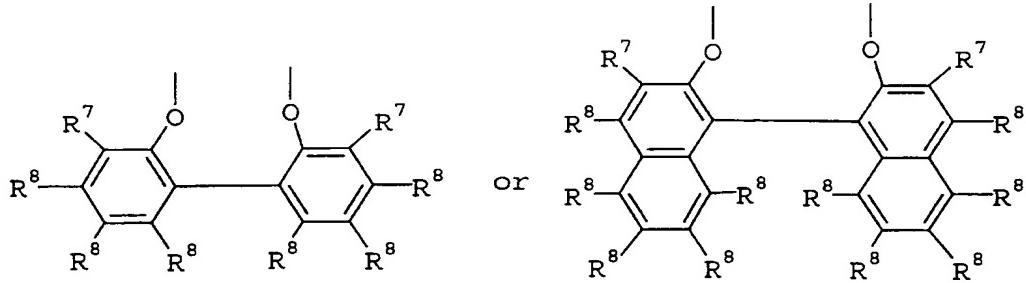
each Z is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)SR⁴, -SR⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, -C(R⁵)=NR⁶, -C(R⁵)=N-O-R⁶, -P(O)(OR⁴)(OR⁴), -S(O)₂R⁴, -S(O)R⁴, -C(O)OC(O)R⁴, -NR⁴CO₂R⁴, -NR⁴C(O)NR⁵R⁶, or -CN;

15 each R⁴ independently is C₁ to C₁₂ alkyl or C₆ to C₂₀ aryl;

each R⁵ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;

20 each R⁶ independently is H, C₁ to C₁₂ alkyl, or C₆ to C₂₀ aryl;

Q is a divalent bridging group of the formula:

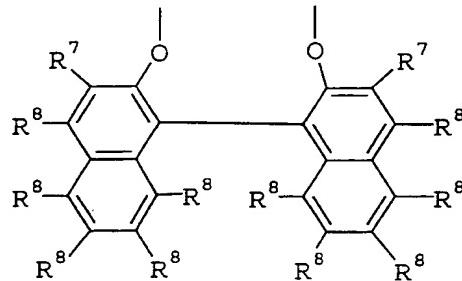


25 wherein:

each R⁷ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, -CF₃, -C(R⁵)=NR⁶, -NR⁵R⁶ or -R³Z; and

30 each R⁸ is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or CF₃.

15. The catalyst composition of claim 14 in which the ligand is of formula I wherein:
- each R¹ independently is -R³Z;
- each R² independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, -OR⁴, -CO₂R⁴, -C(O)R⁴, -CHO, -CN, or -CF₃;
- each R³ independently is C₁ to C₄ alkylene;
- each Z independently is -CO₂R⁴, -CHO, -C(O)R⁴, -C(O)NR⁵R⁶, -OC(O)R⁴, -OC(O)OR⁴, -N=CR⁵R⁶, or -C(R⁵)=NR⁶;
- Q is a divalent bridging group of the formula:



wherein:

- each R⁷ independently is -CO₂R⁴, -C(O)R⁴, -C(R⁵)=N-O-R⁶, -CHO, -CN, or -C(R⁵)=N(R⁶); and
- each R⁸ independently is H, F, Cl, C₁ to C₁₂ alkyl, C₆ to C₂₀ aryl, OR⁴, -CO₂R⁴, -C(O)R⁴, -CN, or -CF₃.

16. The catalyst composition of claim 15 in which each R² is H; each R³ is C₁ to C₃ alkylene; each Z is -CO₂R⁴.
17. The catalyst composition of claim 16 in which the metal is selected from the group consisting of rhodium, cobalt, iridium, palladium, and platinum.
18. The catalyst composition of claim 17 in which the metal is rhodium.

19. The catalyst composition of claim 18 in which the rhodium is in the form of a rhodium hydride, halide, organic acid salt, acetylacetone, inorganic acid salt, oxide, carbonyl compound, or amine compound.

5

20. The catalyst composition of claim 19 in which the rhodium is in the form of rhodium bis(carbonyl)acetylacetone.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/25122

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7	C07F9/145	C07F9/6574	C07C45/50	B01J31/18	C07F9/117
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7	C07F	C07C	B01J
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 33854 A (DSM N.V.) 18 September 1997 (1997-09-18) the whole document ----	1-20
Y	WO 99 06357 A (E.I. DU PONT DE NEMOURS AND CO.) 11 February 1999 (1999-02-11) the whole document ----	1-20
Y	EP 0 839 787 A (DSM N.V.) 6 May 1998 (1998-05-06) the whole document ----	1-20
Y	US 5 910 600 A (HISAO URATA) 8 June 1999 (1999-06-08) cited in the application the whole document -----	1-20

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

7 December 2000

Date of mailing of the international search report

18/12/2000

Name and mailing address of the ISA

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Authorized officer

Beslier, L

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/25122

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
WO 9733854 A	18-09-1997	AU 2045197 A CA 2249026 A DE 69703035 D EP 0888274 A JP 2000506525 T US 6018081 A US 5874641 A			01-10-1997 18-09-1997 12-10-2000 07-01-1999 30-05-2000 25-01-2000 23-02-1999
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US 5910600 A	08-06-1999	BR 9701970 A CN 1167769 A DE 19717359 A JP 10045775 A JP 10045776 A			15-09-1998 17-12-1997 06-11-1997 17-02-1998 17-02-1998